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DATA EVALUATION RECORD

STUDY 4

CHEM 275100 Buprofezin §162-1
CAS No. 69327-76-0
FORMULATION--00--ACTIVE INGREDIENT

STUDY ID 44394042
Singer, S. S. 1996. The degradation of ^{14}C-phenyl buprofezin under aerobic conditions in 2 U.S. soils: sandy loam and sandy clay loam. Laboratory Project ID: 505BF. Unpublished study performed and submitted by AgrEvo USA Co., Pikeville, NC.

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CONCLUSIONS

Metabolism - Aerobic Soil

1. This study is scientifically valid and provides useful information on the aerobic soil metabolism of buprofezin.

2. The study meets Subdivision N Guidelines for the fulfillment of EPA data requirements on aerobic soil metabolism.

3. Uniformly phenyl ring-labeled [^{14}C]buprofezin, at a nominal application rate of 1.9 mg/kg, degraded with a registrant-calculated half-life of 24.4 days (r^2 = 1.0) in sandy loam soil adjusted to 75% of 0.33 bar moisture content and incubated in darkness at 25.1 ± 1 °C for up to 181 days. The half-life was calculated using a nonlinear regression model. Based on reviewer-calculated first and second half-lives, the dissipation appeared to be biphasic. All data, designated as percentages of the applied, are percentages of the nominal application. Based on reverse-phase TLC data, the parent compound was initially 94.7% (1.8 ppm) of the applied radioactivity, decreased to 57.9% (1.1 ppm) by 21 days posttreatment, was 17.7% (0.33 ppm) at 62 days, and was 3.9% (0.07 ppm) at 181 days. No major degradates were detected. The minor degradates BF10, BF12, BF19, and BF22 were each present at ≤0.9% of the applied radioactivity throughout the incubation period. Nonextractable [^{14}C]residues were a maximum of 33.0% of the applied radioactivity at 91 days posttreatment; [^{14}C]residues associated with the fulvic acid, humic acid, and humin fractions were 4.5%, 4.1%, and 12.1% of the applied radioactivity, respectively, at 42 days. Evolved $^{14}CO_2$ accounted for 3.8% of the applied radioactivity by 7 days posttreatment, 39.3% by 62 days, and 60.2% by 181 days.

   Uniformly phenyl ring-labeled [^{14}C]buprofezin, at a nominal application rate of 1.8 mg/kg, degraded with a registrant-calculated half-life of 59.0 days (r^2 = 1.0) in sandy clay loam soil adjusted to 75% of 0.33 bar moisture content and incubated in darkness at 25 ± 1 °C for up to 364 days. The half-life was calculated using a nonlinear regression model. Based on reviewer-calculated first and second half-lives, the dissipation appeared to be biphasic. Based on reverse-phase TLC data, the parent compound was initially 95.4% (1.8 ppm) of the applied radioactivity, decreased to 51.3% (0.94 ppm) by 63 days posttreatment, and was 9.4% (0.17 ppm) at 364 days. No major degradates were detected. The minor degradates BF10, BF12, BF19, and BF22 were present at ≤1.9% of the applied radioactivity throughout the incubation period. Nonextractable [^{14}C]residues were a maximum of 29.9% of the applied radioactivity at 364 days posttreatment; [^{14}C]residues associated with the fulvic acid, humic acid, and humin fractions were 8.6%, 7.3%, and 5.5% of the applied radioactivity, respectively, at 364 days. Evolved $^{14}CO_2$ accounted for 1.5% of the applied radioactivity by 7 days posttreatment, 32.1% by 126 days, and 49.5% by 364 days.

METHODOLOGY

Samples (100 g) of sieved (2 mm) sandy loam soil (collected from Wonder Lake, Illinois; 70.9% sand, 17.9% silt, 11.2% clay, 5.5% organic matter, pH 7.8, CEC 11.5 meq/100 g; Table 1, p. 46) and sandy clay loam (collected from Hale Country, Texas; 58.4% sand, 18.4% silt, 23.2% clay, 1.1% organic matter, pH 7.0, CEC 11.7 meq/100 g) were weighed into silanized flasks and adjusted to 75% of the soil moisture content at 0.33 bar (pp. 19, 21). To determine viability prior to the incubation, soil microbial biomass was measured using the chloroform fumigation method (pp. 19, 35); additionally, to determine viability during the incubation, soil microbial biomass was measured in both the treated and untreated sandy loam soil (114 days) and sandy clay loam soil (182 days). For the metabolism study, the soils were treated with uniformly phenyl ring-labeled [^{14}C]buprofezin {2-[(1,1-dimethylethyl)imino]tetrahydro-3-(1-methylethyl)-5-phenyl-4H-1,3,5,-thiadiazin-4-one; radiochemical purity 97.4%, specific activity 95.1 μCi/mg (sandy loam soil) or radiochemical purity 97.0%, specific activity 101 μCi/mg (sandy clay loam soil); pp. 14-15}, dissolved in acetone, at nominal applications of 1.9 mg/kg (sandy loam soil) and 1.8 mg/kg (sandy clay loam soil; p. 21). The treated soil samples were incubated in darkness at 25 ± 1 °C for up to 181 (sandy loam) or 364 days (sandy clay loam); soil moisture was adjusted to 75% of 0.33 bar as necessary. The flasks were aerated with humidified CO_2-free air; the effluent air was passed through an ethylene glycol trap followed by two ethanolamine traps to capture [^{14}C]volatiles (Figure 1, p. 57). Duplicate samples were removed for analysis at 0, 1, 3, 7, 14, 21, 28, 42, 62, 91, 119, and 181 days posttreatment for the sandy loam soil; and at 0, 3, 7, 14, 21, 28, 42, 63, 98, 126, 154, 183, 280, and 364 days posttreatment for the sandy clay loam soil (p. 22). The volatile traps were sampled and replaced at similar intervals and/or as necessary throughout the incubation period (Appendix III, pp. 87, 88).

The sandy loam soil samples were extracted by shaking with ethyl acetate four times (p. 22). The sandy clay loam soil samples were extracted four times by blending with acetonitrile:water (4:1; v:v). The combined extracts were analyzed for each soil sample by LSC (p. 23); the limit of quantitation was twice background (approximately 60 dpm; p. 34). Following the initial extractions, both soils were subjected to Soxhlet extraction with acetonitrile:water (4:1; v:v) overnight and aliquots of the extract and apparatus rinsate were combined and analyzed by LSC. Additional, more rigorous extraction procedures were applied to selected soil samples following Soxhlet extraction; however, recovery of applied radioactivity was negligible (pp. 24, 25). Nonextractable [^{14}C]residues were determined in subsamples of post-extracted soils by LSC following combustion.

All soil extracts were concentrated by rotary evaporation and analyzed by normal-phase TLC on silica gel plates developed in toluene:ethyl acetate:acetic acid (60:20:1, v:v:v) for parent buprofezin and the degradates BF10, BF12 and BF19; or by reverse-phase TLC on KC18F (Whatman) plates developed in tetrahydrofuran:acetonitrile:water:acetic acid

(25:25:50:0.1, v:v:v:v; plus 1 g NaCl per 100 mL) for the degradate BF22 and other polar degradates. Samples were co-chromatographed with nonradiolabeled reference standards visualized with UV (254 nm) light. Radiolabeled residues were located by autoradiography and quantified by a linear analyzer (pp. 26, 27); the detection limit was approximately 25 dpm (p. 34). Compound identities were confirmed in extracts from selected soil samples by HPLC (Chromegabond C18 column) using a mobile phase gradient of 0.1% acetic acid in water:0.1% acetic acid in acetonitrile (85:15 to 0:100; v:v) with UV detection and radioactive flow detection (p. 28); samples were co-chromatographed with non-radiolabeled reference standards. Fractions from HPLC analysis were collected and analyzed by LSC. Compounds were identified by comparing their retention time with that of a co-eluting standard using UV and radioactive traces.

Total [^{14}C]radioactivity in the volatile traps was determined by LSC. Evolved $^{14}CO_2$ was confirmed in selected samples of the ethanolamine trap solutions. An aliquot of the trap solution was added to a reaction vessel with $NaHCO_3$ and NaOH. The solution was stirred and slowly acidified (pH < 3) with 4 M HCl. Evolved $^{14}CO_2$ was captured in two NaOH traps and an ethanolamine or ethylene glycol trap; total [^{14}C]radioactivity was determined by LSC. Evolved $^{14}CO_2$ was confirmed in the first NaOH trap by precipitation using barium chloride and LSC analysis of the supernatant (pp. 28, 29).

To determine bound residues associated with humic acid, fulvic acid and humin fractions, subsamples (5 g) of post-extracted soil were refluxed with 0.25 *N* HCl for one hour (pp. 24, 25). The extract was separated and partitioned twice with ethyl acetate and analyzed by LSC. The remaining sediment was then shaken for 24 hours in 0.5 *N* NaOH. The extract was separated from the sediment, acidified (pH 1 with concentrated HCl), and centrifuged to separate the precipitate. The supernatant was decanted and analyzed by LSC (fulvic acid fraction). The precipitate was redissolved with 0.5 *N* NaOH and analyzed by LSC (humic acid fraction). The remaining [^{14}C]residues (humin fraction) in the sediment were determined by LSC following combustion.

DATA SUMMARY

Sandy Loam Soil

Uniformly phenyl ring-labeled [^{14}C]buprofezin (radiochemical purity 97.4%), at a nominal application rate of 1.9 mg/kg, degraded with a registrant-calculated half-life of 24.4 days (r^2 = 1.0) in sandy loam soil adjusted to 75% of 0.33 bar moisture content and incubated in darkness at 25.1 ± 1 °C for up to 181 days (p. 39; Figure 7, p. 63). The half-life was calculated using a nonlinear regression model. Based on reviewer-calculated first and second half-lives, the dissipation appeared to be biphasic (see Comment #2). All data, designated as percentages of the applied, represent percentages of the nominal application. Based on reverse-phase TLC data, the parent compound was initially present

at 94.7% (1.8 ppm) of the applied radioactivity, decreased to 57.9% (1.1 ppm) by 21 days posttreatment, and 44.7% (0.84 ppm) by 28 days, was 17.7% (0.33 ppm) at 62 days, and was 3.9% (0.07 ppm) at 181 days (Table 6, p. 51). No major degradates were detected. The minor degradates BF10, BF12, BF19, and BF22 were each present at ≤0.9% of the applied radioactivity throughout the incubation period. Nonextractable [^{14}C]residues were 12.5-14.7% of the applied radioactivity from 14 to 28 days posttreatment and were 29.7-33.0% from 42 to 181 days (Table 2, p. 47); [^{14}C]residues associated with the fulvic acid, humic acid, and humin fractions were 4.5%, 4.1%, and 12.1% of the applied radioactivity, respectively, at 42 days posttreatment (p. 43). Evolved $^{14}CO_2$ accounted for 3.8% of the applied radioactivity by 7 days posttreatment, 39.3% by 62 days, and 60.2% by 181 days.

Material balances (based on LSC analysis for individual replicates) were 87.6-103.2% of the applied radioactivity throughout the incubation period, with no clear pattern of loss (Table 2, p. 47).

Sandy Clay Loam Soil

Uniformly phenyl ring-labeled [^{14}C]buprofezin, at a nominal application rate of 1.8 mg/kg, degraded with a registrant-calculated half-life of 59.0 days (r^2 = 1.0) in sandy clay loam soil adjusted to 75% of 0.33 bar moisture content and incubated in darkness at 25 ± 1 °C for up to 364 days (p. 39; Figure 7, p. 63). The half-life was calculated using a nonlinear regression model. Based on reviewer-calculated first and second half-lives, the dissipation appeared to be biphasic (see Comment #2). Based on reverse-phase TLC data, the parent compound was initially present at 95.4% (1.8 ppm) of the applied radioactivity, decreased to 51.3% (0.94 ppm) by 63 days posttreatment, and 24.4% (0.45 ppm) by 126 days, and was 9.4% (0.17 ppm) at 364 days (Table 7, p. 52). No major degradates were detected. The minor degradates BF10, BF12, BF19, and BF22 were each present at ≤1.9% of the applied radioactivity throughout the incubation period. Nonextractable [^{14}C]residues were 12.7% of the applied radioactivity at 42 days posttreatment and were 29.9% at 364 days (Table 3, p. 48); [^{14}C]residues associated with the fulvic acid, humic acid, and humin fractions were 8.6%, 7.3%, and 5.5% of the applied radioactivity, respectively, at 364 days posttreatment (p. 43). Evolved $^{14}CO_2$ accounted for 1.5% of the applied radioactivity by 7 days posttreatment, 32.1% by 126 days, and 49.5% by 364 days.

Material balances (based on LSC analysis for individual replicates) were 88.1-100.1% of the applied radioactivity throughout the incubation period, with no clear pattern of loss (Table 3, p. 48).

COMMENTS

1. The reviewer notes that the study was conducted at an exaggerated dose rate. The treatment rate (1.8-1.9 mg/kg) was reported to be greater than two times the maximum label rate (1.5 lb a.i./A) for the parent (p. 20). While exaggerated rate studies may be used to facilitate the identification of degradates, EPA requires that kinetics studies be conducted with the maximum dose rate, as stated in the *U.S. EPA Rejection Rate Analysis - Environmental Fate Guideline Issues* (EPA 738-R-93-010; 1993).

2. The reviewer notes that the degradation pattern of buprofezin in the test soils was biphasic. The reviewer calculated first half-lives of 24.9 days ($r^2 = 0.99$; 0-62 day data) and 66.0 days ($r^2 = 0.99$; 0-126 day data) in the sandy loam and sandy clay loam soils, respectively. Buprofezin degraded with reviewer-calculated second half-lives of 58.2 days ($r^2 = 0.97$; 62-181 day data) and 182.4 days ($r^2 = 0.98$; 126-364 day data) in the sandy loam and sandy clay loam soils, respectively.

3. The study was conducted using uniformly phenyl ring-labeled [^{14}C]buprofezin. The compound contained an additional ring structure that was not radiolabeled. An additional study using the compound radiolabeled in the second ring structure may not be necessary because the proposed metabolic pathway indicated that degradates containing only the second ring structure (i.e., without the phenyl ring) would not form and all of the degradates would eventually metabolize to CO_2 (Figure 22, p. 78). The reviewer noted that major degradates were not detected in either of the soils and that evolved CO_2 accounted for 60.2% and 49.5% of the applied radioactivity at study termination for the sandy loam and sandy clay loam soil systems, respectively (Tables 2, 3; pp. 47, 48).

4. The soil series names were not reported as required by Subdivision N Guidelines.

5. The abstract incorrectly stated the buprofezin half-life in sandy loam soil as 22.4 days (p. 6). The correct half-life was 24.4 days (p. 39).